of 8 and 7, respectively, over palladium on carbon.

The formation of 5, 6, and 7 could be understood if 8 were an intermediate that reacted as outlined in Scheme II. Indeed, treatment of 8 with lithium aluminium hydride did afford 5, 6, and 7 in comparable ratios.

Further justification of the ideas in Scheme II rested on the assumption that reduction at C-4 of 3 would be the first event and that the resulting product 4 would collapse under the pressures depicted in Scheme III. The departure of the methoxy group is facilitated by complexation with a trivalent aluminum species[16] and is triggered by synchronous hydride-induced cleavage of the siloxy bond.[18] In order to test this notion, 4 was obtained from 3 in 95% yield by reduction with sodium borohydride. When 4 was not subjected to lithium aluminum hydride, 5, 6, and 7 were indeed obtained in the required ratios, therefore giving substance to the sequence in Scheme II.

The foregoing observations are particularly significant for compounds that bear sensitive functional groups, and which therefore cannot withstand the acidic conditions required for unveiling the latent enone.[6,8,10] Thus, hydrolysis of 4 at pH 3 afforded only a 25% yield of **8a**. Even under these mild conditions there was great loss of the glycosidic methoxyl. On the other hand, the route **3** → **7** → **8a** proceeded in 60% overall yield. This latter sequence *is, therefore, much better for such acid-sensitive molecules in spite of the fact that an extra step is required.*

Acknowledgment. We are grateful to Professor Danishefsky of Yale University and Professor Stork of Columbia for helpful discussions.

Registry No. 1, 71049-77-9; 2, 71735-01-8; 3 (isomer 1), 89828-00-2; 3 (isomer 2), 89828-01-3; 4, 89828-07-9; 5, 89828-02-4; 6, 89828-03-5; 7, 89828-04-6; 8a, 89828-05-7; 8b, 89828-06-8.

Supplementary Material Available: Experimental procedures and spectral data for compounds 3, 6, 7, and 8a (3 pages). Ordering information is given on any current masthead page.

(16) A precedent of sorts for this process may be found in the lithium aluminum hydride reduction of a β-dicarbonyl intermediate in Stork's synthesis of cedrol.[17]

(17) Stork, G.; Clarke, F. H. *J. Am. Chem. Soc.* **1961**, *83*, 3114.

(18) For a recent instance of cleavage of trimethylsilyl ether by lithium aluminum hydride, see ref 19.

(19) Beely, N. R. A.; Cremer, G.; Dorlhene, A.; Mompom, B.; Pascard, C.; Dau, E. T. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1046.

Bert Fraser-Reid,*[1] Md. Abdur Rahman
D. R. Kelly,[2] R. M. Srivastava[3]
Chemistry Department, University of Maryland
College Park, Maryland 20472
and Gross Chemical Laboratory, Duke University
Durham, North Carolina 27706[4]
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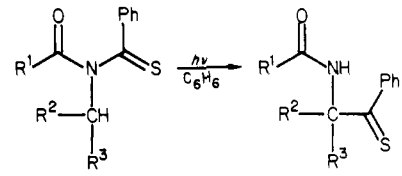
Photochemical Reactions of Acyclic Monothioimides. A Novel Photorearrangement Involving 1,2-Thiobenzoyl Shift

Summary: Photolysis of *N*-acylthiobenzamides in benzene gave thioketones via a novel photorearrangement involving 1,2-thiobenzoyl shift; the formation of the products was explainable in terms of β-hydrogen abstraction by the thiocarbonyl group.

Sir: Although the photoreactions of thioketones[1] and thioesters[2] are well studied, those of thioimides have not been reported except for [2 + 2] cycloaddition of cyclic thioimides with olefines.[3] In relation to our previous studies on photochemical reactions of nitrogen-containing thiocarbonyl compounds[4] and acyclic imides,[5] we now report the photorearrangement of *N*-acylthiobenzamide 1, which involves an unprecedented 1,2-thiobenzoyl shift.

Table I. Photolysis of 1



	R¹	R²	R³	yield, %
a	Ph	Me	Me	62
b	Ph	Me	Et	80
c	Ph	Me	Ph	98
d	Me	Me	Me	64
e	Me	Me	Ph	95
f	Ph	H	Ph	43
g	Ph	H	*i*-Pr	0

The monothioimides **1a–g** were obtained almost quantitatively by acylation of the corresponding *N*-alkylthiobenzamides. The structure of these compounds was determined by the elemental analyses and spectral data. The visible spectrum of the monothioimide **1a** in *n*-hexane showed a maximum at 456 nm (ε 160) assignable to nπ* band of the thiocarbonyl group. Irradiation of *N*-isopropyl-*N*-benzoylthiobenzamide (**1a**) in benzene with a high-pressure mercury lamp under argon gave α-(benzoylamino)isobutyrothiophenone (**2a**) in 62% yield. The structure of **2a** was determined by the elemental analysis and spectra data. The IR spectrum (KBr) exhibited absorptions at 3260 (NH), 1630 (C=O), 1525 [C(=O)NH], and 1055 cm^{-1} (C=S). The mass spectrum showed the molecular peak at *m/e* 283 (M^+), and fragment peaks at *m/e* 187 (M – PhC=O), 163 [PhC(=S)C$(CH_3)_2$], 162 (M – PhC=S), 121 (PhC=S), and 105 (PhC=O). The ^1H NMR spectrum ($CDCl_3$) showed signals at δ 1.90 (s, 6 H, 2 × CH_3), 7.2–7.5 (m, 8 H, Ph), 7.6–7.8 (m, 2 H, Ph), and 7.9 (br, 1 H, NH). The ^{13}C NMR exhibited signals at δ 27.8 (q), 68.5 (s), 125.9 (d), 126.9 (d), 127.5 (d), 128.4 (d), 129.2 (d), 131.4 (d), 135.2 (s), 141.8 (s), 166.2 (s), and 255.6 (s). Furthermore, the visible spectrum of **2a** showed a maximum at 524 nm (ε 90) assignable to the nπ* band of thioketone moiety. Photolysis of other thioimides under the same conditions also gave the corresponding thio-

(1) (a) Ohnishi, Y.; Ohno, *A. Bull. Chem. Soc. Jpn.* **1973**, *46*, 3868. (b) Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125 and references cited therein. (c) Ho, K. W.; de Mayo, P. *J. Am. Chem. Soc.* **1979**, *101*, 5725 and references cited therein. (d) Muthuramu, K.; Sundari, B.; Ramamurthy, V. *Tetrahedron* **1983**, *39*, 2719 and references cited therein. (e) Blackwell, D. S. L.; de Mayo, P. *J. Chem. Soc., Chem. Commun.* **1973**, 130. (f) Couture, A.; Gomez, J.; de Mayo, P. *J. Org. Chem.* **1981**, *46*, 2010 and references cited therein.

(2) (a) Achmatowicz, S.; Barton, D. H. R.; Magnus, P. D.; Poulton, G. A.; West, P. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1567 and 1580. (b) Ohno, A.; Koizumi, T.; Akasaki, Y. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 319 and references cited therein. (c) Ogata, Y.; Takagi, K.; Ihda, S., *J. Chem. Soc., Perkin Trans. 1* **1975**, 1725.

(3) Oda, K.; Yoshida, E.; Wakao, S.; Matsuda, M.; Kanaoka, Y., The 11th Symposium on Organic Sulfur and Phosphorus Chemistry, Tsukuba, Japan, 1983. Added in proof. See also: Sakamoto, M.; Omote, Y.; Aoyama, H. *J. Org. Chem.* **1984**, *49*, 396.

(4) Aoyama, H.; Sakamoto, M.; Omote, Y., *Chem. Lett.* **1983**, 1397.

(5) (a) Aoyama, H.; Sakamoto, M.; Omote, Y., *J. Chem. Soc., Chem. Commun.* **1982**, 119. (b) Aoyama, H.; Sakamoto, M.; Omote, Y. *Chem. Lett.* **1982**, 1211. (c) Aoyama, H.; Sakamoto, M.; Omote, Y. *Tetrahedron Lett.* **1983**, *24*, 1169.

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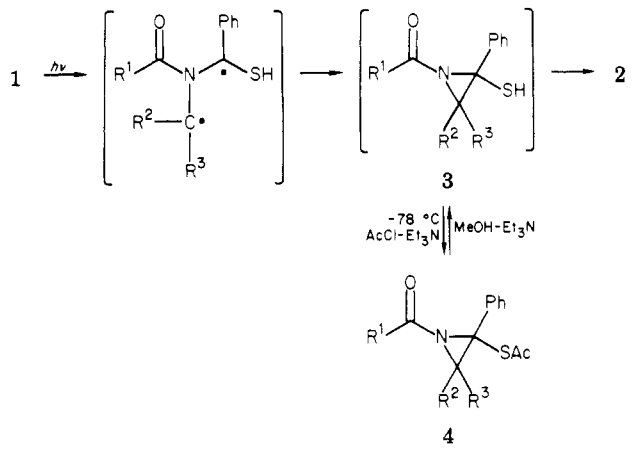
Scheme I



ketones **2b–e** in good yields as shown in Table I. Although photolysis of **1f** also gave the thioketone **2f** in 43% yield, this compound was unstable and decomposed gradually even at room temperature. The photoreaction of **1g** was much slower than that of other monothioimides (**1a–f**), and prolonged irradiation gave an intractable mixture.

The formation of the thioketones **2** is reasonably explained in terms of ring opening of an aziridine (**3**), which is produced by cyclization of **1** (Scheme I). The intermediacy of **3** was confirmed by the following experiments. Irradiation of **1c** in toluene at −78 °C resulted in the loss of the red thioimide color. On warming to room temperature, the colorless solution turned purple and **2c** was obtained as a main product. This finding indicated the presence of an intermediate that did not possess a thiobenzoyl moiety. When the colorless solution obtained in the low-temperature photolysis was treated with acetyl chloride in the presence of triethylamine at −78 °C, 2,3-diphenyl-2-(acetylthio)-1-benzoyl-3-methylaziridine (**4c**, 85%) was obtained, accompanied by a small amount of **2c** (9%). The structure of **4b** was assigned on the basis of elemental analysis and spectral data. The IR spectrum (KBr) exhibited carbonyl frequencies at 1705 and 1660 cm^{-1}. The ^1H NMR spectrum ($CDCl_3$) showed signals at δ 1.14 (s, 3 H, CH_3), 2.01 (s, 3 H, C(=O)CH_3), 7.3–7.8 (m, 13 H, Ph), and 8.1–8.2 (m, 2 H, Ph), and ^{13}C NMR exhibited resonances at 26.3 (q), 31.3 (q), 80.6 (s), 104.7 (s), 126.6 (d), 127.7 (d), 128.0 (d), 128.5 (d), 128.6 (d), 131.9 (s), 139.0 (s), 140.9 (s), 161.6 (s), and 191.8 (s) ppm. The mass spectrum showed molecular ion at m/z 387 (M^+) and fragment peaks at m/e 312 [M − SC(=O)Me], and 207 [M − SC(=O)Me − PhC(=O)]. Furthermore, the fact that the base-catalyzed methanolysis (MeOH–NEt_3) of **4b** gives **2b** almost quantitatively is also consistent with the mechanism shown in Scheme I.

β-Hydrogen abstraction appears to be very rare occurrance in carbonyl photochemitry, giving precedence to the Norrish type II, intermolecular hydrogen abstraction or simply other photochemical reactions.[6] Although a few instances of β-hydrogen abstraction of thioketones have been reported,[1e,f] they are limited to thiones where only β-hydrogens are abstractable or β-hydrogens are strongly activated by substituents. The present photorearrangement involving unprecedented 1,2-thiobenzoyl shift also provides the first example of β-hydrogen abstraction of thioimides.

(6) (a) Padwa, A.; Gruber, R. *J. Am. Chem. Soc.* **1970**, *92*, 107. (b) Padwa, A.; Eisenhardt, W. *Ibid.* **1971**, *93*, 1400. (c) Cormier, R. A.; Schreiber, W. L.; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* **1972**, 729. (d) Scheffer, J. R.; Bhandari, K. S.; Gaylar, R. E., *J. Am. Chem. Soc.* **1975**, *97*, 2178.

Registry No. **1a**, 89873-85-8; **1b**, 89873-86-9; **1c**, 89873-87-0; **1d**, 89873-88-1; **1e**, 89873-89-2; **1f**, 49590-28-5; **1g**, 89873-90-5; **2a**, 89873-91-6; **2b**, 89873-92-7; **2c**, 89873-93-8; **2d**, 89873-94-9; **2e**, 89873-95-0; **2f**, 89873-96-1; **4a**, 89873-98-3; **4b**, 89873-99-4; **4c**, 89873-97-2; **4d**, 89874-00-0; **4e**, 89874-01-1; **4f**, 89874-02-2; hydrogen, 1333-74-0.

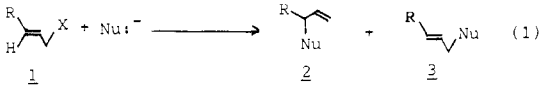
Supplementary Material Available: Experimental procedures and spectral data of starting materials and photoproducts are described (2 pages). Ordering information is given on any current masthead page.

Masami Sakamoto, Hiromu Aoyama*
Yoshimori Omote
Department of Chemistry, The University of Tsukuba
Sakura-mura, Ibaraki, 305 Japan
Received December 27, 1983

Regiospecific Alkylation on Allylic Halides with Latent γ-Functionality

Summary: Completely regiospecific alkylation on stereospecifically γ-silylated allylic bromides was achieved with a variety of anionic nucleophiles of a wide range of strength.

Sir: Advantageous aspects of using electrophilic allylic reactants in organic synthesis can never be underestimated because they are more reactive than the corresponding saturated analogues, and their obvious precursors, the corresponding allylic alcohols, can be prepared stereospecially.[1] But development of allylation reactions possessing high regio- and stereoselectivities has been a long-standing problem in organic chemistry, mainly because of the preponderant S_N2', reactions especially with strong nucleophiles (eq 1), and numerous attempts to control the site of reaction have been made.[1]



Herein is reported a solution for this problem in which by placing a sterically demanding proton equivalent on the γ-position of the allylic halide **1** or the corresponding stereoisomer, the unwanted reaction at γ-position (S_N2') is curtailed. Additionally, if the allylic reactants would be available and the proton equivalent is removed (or replaced by other funtionality), both stereospecifically, this method would render a general synthesis of alkenes. To this end, a trialkylsilyl group would be a perfect choice for the requirements.[2]

Consequently, a number of stereospecifically 3-trimethylsilylated allylic alcohols **4** and **5** were prepared[3,4]

(1) (a) Magid, R. M. *Tetrahedron*, **1980**, *36*, 1901. (b) Calo, V.; Lopez, L.; Pesce, G.; Calianno, A. *J. Org. Chem.* **1982**, *47*, 4482. (c) Goering, H. L.; Kantner, S. S.; Tseng, C. C. *Ibid.* **1983**, *48*, 715.

(2) For reviews of organosilicon chemistry, see: Colvin, E. W. *Chem. Soc. Rev.* **1978**, *7*, 15. "Silicon in Organic Synthesis"; Butterworth: London, 1981. Paquette, L. A. *Science (Washington, D.C.)* **1982**, *217*, 1793. Chan, T. H. *Acc. Chem. Res.* **1977**, *10*, 442. Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983.

(3) 3(*E*)-(Trimethylsilyl)allylic alcohols **4** were prepared by either of the following methods. (a) Titanocene dichloride catalyzed syn-hydromagnesiation of propargylic alcohols (Sato, F.; Ishikawa, H.; Watanabe, H.; Miyake, T.; Sato, M. *J. Chem. Soc., Chem. Commun.* **1981**, 718), followed by trimethylsilylation with trimethylsilyl chloride in the presence of HMPT. (b) Hydroalumination ($LiAlH_4$–NaOMe)–iodination of 3-(trimethylsilyl)-2-propyn-1-ol, followed by cuprate reaction on the 3-(*E*)-iodoallylic alcohols (Corey, E. J.; Katzenellenbogen, J. A.; Gilman, N. W.; Roman, S. A.; Erickson, B. W. *J. Am. Chem. Soc.* **1968**, *90*, 5618).

0022-3263/84/1949-1838$01.50/0